U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-281 370

Volatility of Mercury from Soils Amended with Various Mercury Compounds

Environmental Monitoring and Support Lab, Las Vegas, Nev

Apr 78

PB 281 370

EPA-600/3-78-046
April 1978

Ecological Research Series

VOLATILITY OF MERCURY FROM SOILS AMENDED WITH VARIOUS MERCURY COMPOUNDS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximim interface in related fields. The nine sereies are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy—Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans,plant and animal species, and materials. Problems are assessed for their long-and short-term influences. Investigations include formations, transport, and pathway studies to determine the fate of pollutants and their effects. This work provided the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-78-046		PB281370

4. TITLE AND SUBTITLE	5. REPORT DATE
VOLATILITY OF MERCURY FROM SOILS AMENDED WITH VARIOUS MERCURY COMPOUNDS	April 1978
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert D. Rogers	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Las Vegas, Nevada 89114	1AA602
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Las Vegas, NV Office of Research and Development Environmental Monitoring and Support Laboratory Las Vegas, Nevada 89114	Final
	14. SPONSORING AGENCY CODE EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A study was conducted to determine the rate of mercury volatilization from soils freshly amended with mercury compounds. Mercuric nitrate, mercuric chloride, mercuric acetate, mercuric oxide, and mercuric sulfide were used in conjunction with three soils: a loamy sand, a sand loam, and a clay loam. Mercury was evolved from all combinations and was shown to be dependent upon the solubility of the mercury compound and the texture of the soil.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
mercury mercury volatilization soil chemistry	mercury vapor collection mercury transformation mercuric nitrate mercuric chloride mercuric acetate mercuric oxide mercuric sulfide	07B 07D 08M 18B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	15
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE A02-A01

EPA Form 2220-1 (9-73)

*U.S. GOVERNMENT PRINTING OFFICE: 1978 - 785-724/1902M, 1170, 9-I

EPA-600/3-78-046
April 1978

VOLATILITY OF MERCURY FROM SOILS AMENDED WITH VARIOUS MERCURY COMPOUNDS

By
Robert D. Rogers
Monitoring Systems Research and Development Division
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
LAS VEGAS, NEVADA 89114

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory--Las Vegas, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This study was conducted to determine the rate of mercury volatilization from soils freshly amended with mercury. Different mercury compounds were used in conjunction with three different soil types. Mercury was evolved from all treatments but volatilization was dependent upon the solubility of the mercury compound and the texture of the soil. The conclusions can be beneficial in designing experiments dealing with mercury compounds and soils and also in the interpretation of data gathered by other investigators. Users who should find the report of value include the Office of Air Programs, Office of Toxic Substances, laboratories within the Office of Research and Development, other Federal agencies, and university and industrial research staffs.

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada

ABSTRACT

A study was conducted to determine the rate of mercury volatilization from soils freshly amended with mercury compounds. Mercuric nitrate, mercuric chloride, mercuric acetate, mercuric oxide, and mercuric sulfide were used in conjunction with three soils: a loamy sand, a sand loam, and a clay loam. Mercury was evolved from all combinations and was shown to be dependent upon the solubility of the mercury compound and the texture of the soil.

INTRODUCTION

Studies involving the transformation and fate of mercury (Hg) in the environment have been intensely pursued in recent years. Investigations have been conducted involving both aquatic and terrestrial environments in which mercuric ion (Hg^{++}) is added to the environment of interest and its transformation with time is determined. One transformation which is often overlooked is that Hg^{++} can rapidly be reduced and lost from the study system as elemental Hg.

Some work on the volatilization of reduced Hg^{++} from aquatic systems has been conducted (Avotins and Jenne, 1975), and it has also been noted that Hg applied to soil can be volatilized as elemental Hg (Alberts et al., 1974; Kimura and Miller, 1964; Hitchcock and Zimmerman, 1957). However, since large losses of Hg have not been suspected, no effort has generally been made to monitor the amount of Hg liberated from either deliberately or accidentally contaminated soils. In addition, work is necessary to determine the actual loss rate of Hg from several soil types as a function of various inorganic mercuric sources.

Because of the need for more information, a study was conducted to determine the effect of inorganic mercuric sources on Hg volatilization from soil. Since the possibility exists that soil type could influence Hg loss, because of chemical and/or physical properties, three different soil types were amended with solutions of a variety of inorganic mercury compounds.

CONCLUSIONS

The following conclusions can be drawn from the study:

1. Considerable amounts of Hg can be volatilized from soil but the loss depends on the soil type and the inorganic form of Hg used. These data indicate that mercury can be volatilized from soil amended with any of the water-soluble Hg compounds used.

2. The maximum loss of Hg occurred within the first week after amendment of the soil with such Hg compounds.

RECOMMENDATIONS FOR FUTURE RESEARCH

Future work to determine the mechanism causing volatilization of Hg applied to soil is needed.

MATERIALS AND METHODS

Three soils, a loamy sand, a sandy loam, and a clay loam, were used for this study. They were collected from an agricultural area in southern Nevada. Depth of the soil collections was limited to the upper 10 centimeters of the Ap horizon (plow layer). The moist soil was processed through a 2-millimeter sieve and stored at room temperature in plastic bags. The physical and chemical properties of the soils are found in Table 1.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF SOIL

Soil (Texture classification)	Series	Sand	Clay	Organic carbon	Cation exchange capacity	pH
		%			meq/100g	
Sand (Loamy sand)	Bluepoint--a member of the mixed, thermic family of Typic Torripsamment	79.8	3.5	0.53	4.3	9.0
Loam (Fine sandy loam)	Calico--a member of the coarse-loamy, over clayey, mixed (calcareous), thermic family of Aquic Xero-fluvents	53.9	10.8	1.30	12.7	8.6
Clay (Silty clay loam)	Overton--a member of the fine montmoril-lonitic, calcareous, thermic family of Mollic Haplaquepts	14.7	34.4	3.44	29.0	7.8

Five different Hg compounds were used as Hg sources. These included mercuric nitrate [$Hg(NO_3)_2$], mercuric chloride ($HgCl_2$), mercuric acetate [$Hg(C_2H_3O_2)_2$], mercuric oxide (HgO), and mercuric sulfide (HgS). All were soluble in water except HgS which was made up in 0.1N (Na_2S) sodium sulfide. To each soil (50 grams), 50 micrograms of Hg in the desired compound was

added and stirred. This resulted in a concentration of 1 part per million Hg in each soil. The study was arranged so that the three soils were amended with the same Hg compound for the ensuing week's study. In all cases the studies were carried out in triplicate.

After the soil was poured into a flask it was amended with Hg and sufficient water was then added to bring the moisture content to 50% of the soil's moisture holding capacity. The moistened soil was thoroughly mixed and care was taken to prevent soil from being spread on the sides of the flask. A rubber stopper containing connections for inlet and outlet air lines was used to cap the flask. The flasks were connected to an air supply manifold and the outlet was connected to a mercury adsorption trap. Air flow through the flasks was maintained at 20 cubic centimeters per minute. All soils were incubated inside a darkened growth chamber maintained at 25° C.

Mercury adsorption traps were made from 1-milliliter volumetric pipets cut to length with the bulb being filled with gold-coated 40/60-mesh glass beads. The beads were coated using the method of Braman and Johnson (1974). To determine the amount of mercury being volatilized, a clean trap was placed in the exit flow from the flask and after 1 hour the trap was replaced with another trap to safely contain the vented Hg until time for the next 1-hour collection.

Analysis for Hg was carried out by heating the collection traps to 600° C in a block heater. After the trap had been heated for 30 seconds, the desorbed Hg was flushed from the trap with helium into a Hg detector. The detector used in this study was an Isotope Zeeman Atomic Absorption Spectrophotometer (IZAA) (Hadeishi and McLaughlin, 1975).

Analyses were performed in triplicate for each soil treatment. Results for the replicate treatments agreed within 10% and were averaged and expressed as nanograms of Hg evolved per hour.

RESULTS AND DISCUSSION

Mercury was volatilized from soil amended with the different Hg compounds, but the amount volatilized appeared to be affected by the solubility of the compounds (Table 2). Over a 144-hour period of time the three Hg compounds most soluble in water [i.e., $Hg(NO_3)_2$, $HgCl_2$, and $Hg(C_2H_3O_2)_2$] had a greater loss of Hg from the three soils (12 to 38%) followed by the less soluble HgO (6 to 19%) with the insoluble HgS losing only a minor amount of applied Hg (0.2 to 0.3%). These data also indicate that the form of Hg added to the soil has an effect on the initial volatilization of applied Hg.

In all cases the Hg volatilization rate for all treatments, except the HgS, decreased to a minimum within the first week after amendment (Figures 1 through 4). However, in the case of the HgS amended soils, there was minimal volatilization throughout the duration of the study. Whether the decrease in Hg volatilization was due to the loss of a soluble Hg fraction

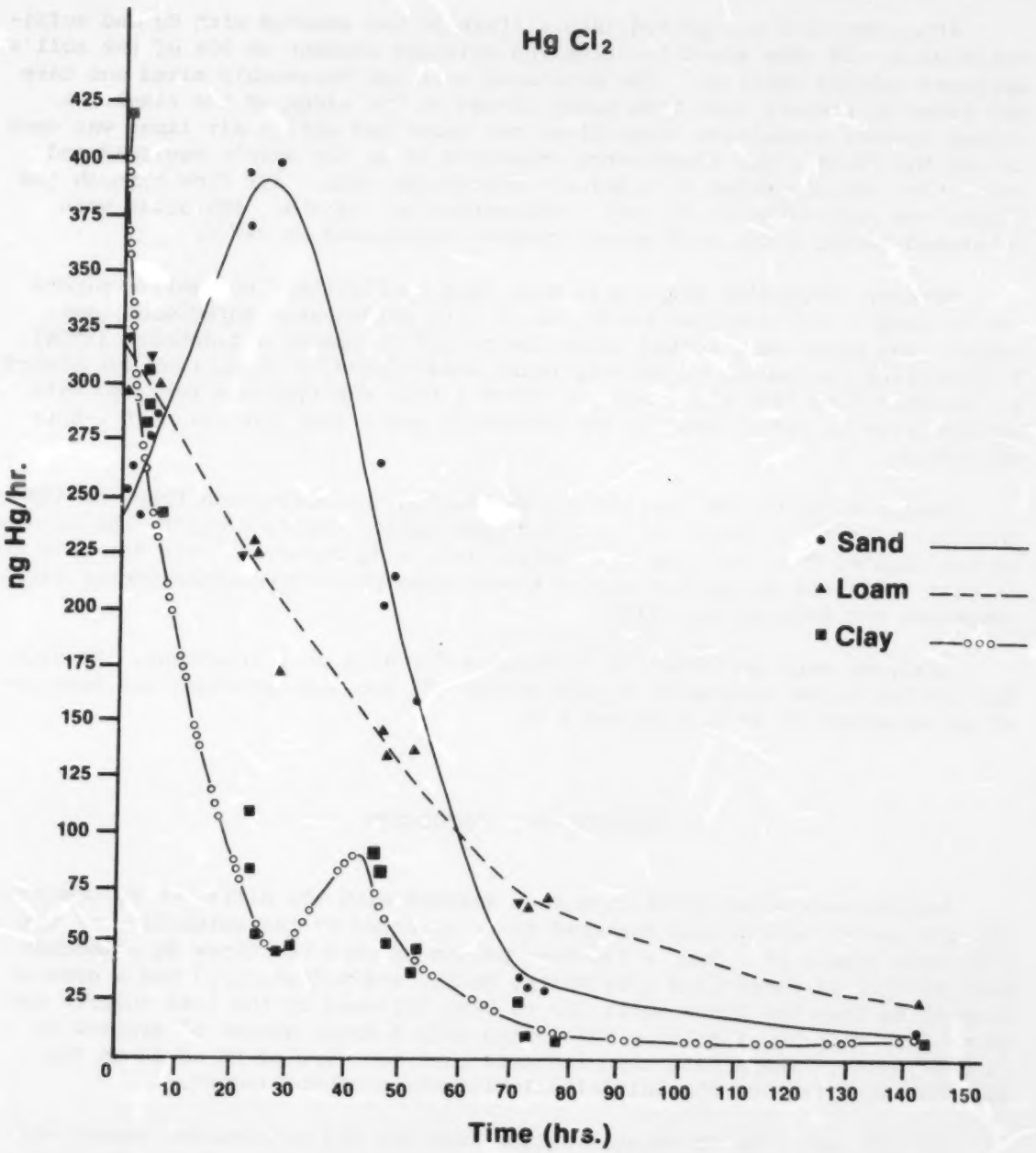

Figure 1. Evolution of Hg from soils amended to 1 ppm Hg with $HgCl_2$.

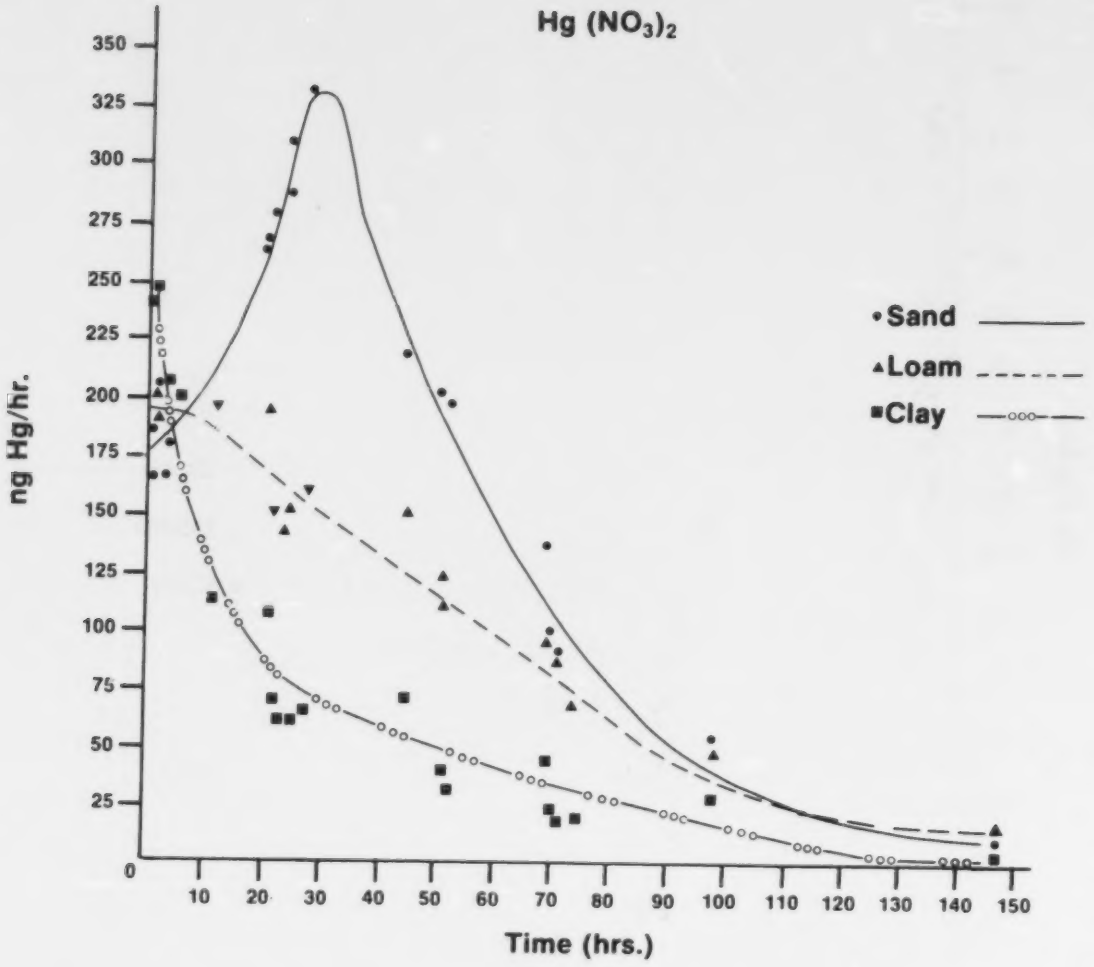

Figure 2. Evolution of Hg from soils amended to 1 ppm Hg with $Hg(NO_3)_2$.

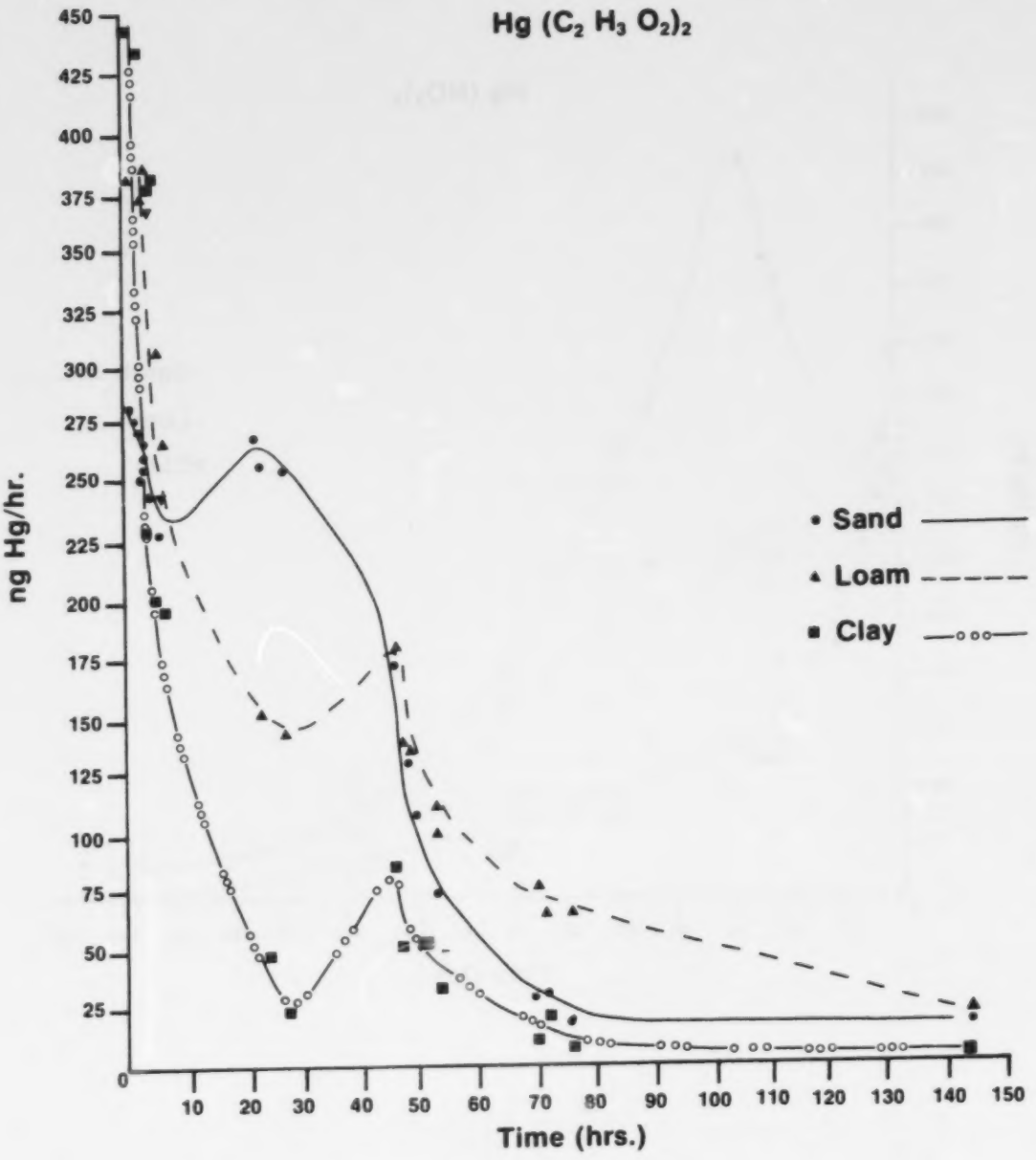

Figure 3. Evolution of Hg from soils amended to 1 ppm Hg with $Hg(C_2H_3O_2)_2$.

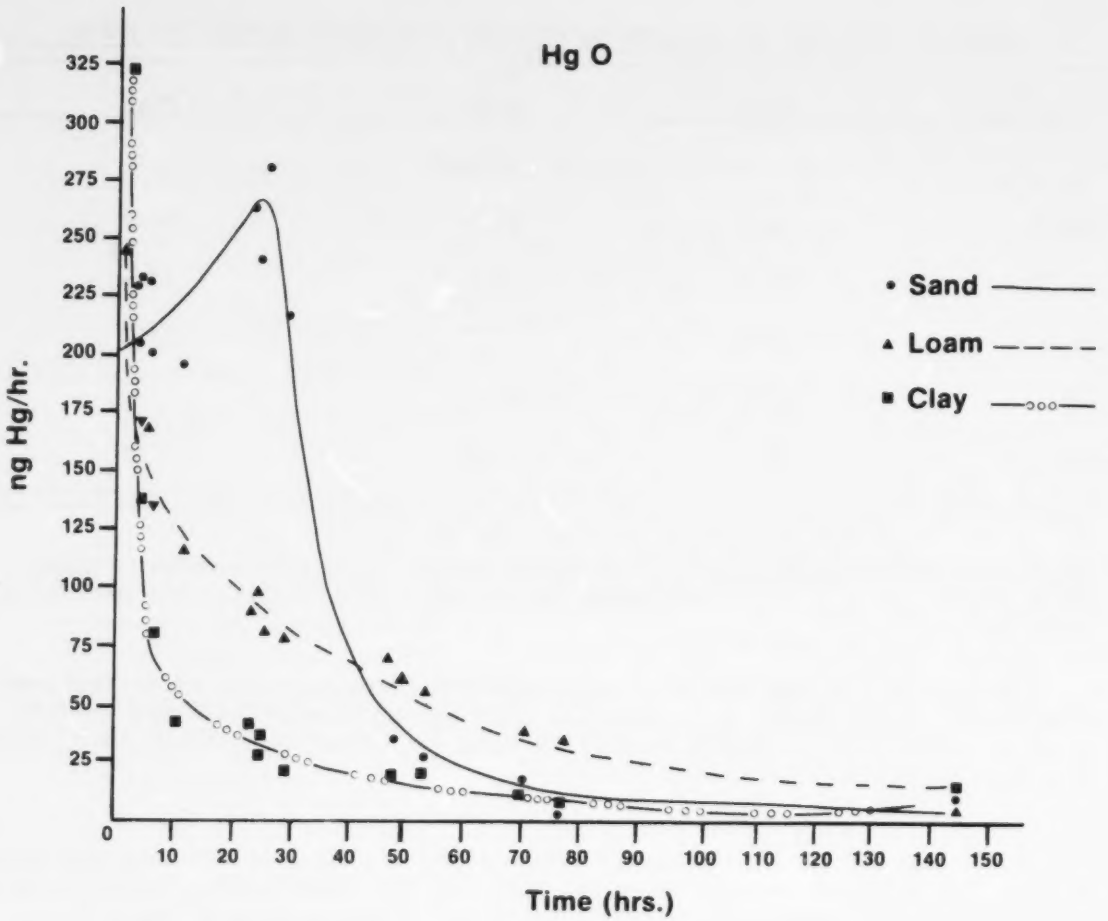

Figure 4. Evolution of Hg from soils amended to 1 ppm Hg with Hg0.

or was the result of the Hg becoming more bound with time could not be determined with this experiment.

The type of soil had a distinct effect on the amount of mercury volatilized. In all cases except sand and loam soils amended with $Hg(C_2H_3O_2)_2$ and the HgS amended soils, the loss rates were sand>loam>clay (Table 2).

TABLE 2. PERCENT OF APPLIED Hg EVOLVED FROM SOILS WITHIN 144 HOURS

Hg Compound	Soil		
	Sand	Loam	Clay
		% evolved	
$HgCl_2$	38.3	32.9	14.2
$Hg(NO_3)_2$	36.5	24.1	13.4
$Hg(C_2H_3O_2)_2$	26.4	30.5	12.1
HgO	19.6	15.0	6.4
HgS	0.2	0.3	0.2

These soils decreased in clay and organic matter in the same order. Since Hg is bound to both clay and organic matter this could explain the decreased volatility.

With both the loam and clay soil, maximum volatilization of Hg followed immediately after amendment. However, with the sand soil there was a 22 to 29-hour lag before a maximum volatility rate was obtained. The cause of this phenomenon was not ascertained.

This study amply shows that substantial quantities of Hg can be lost due to volatilization from soils amended with a variety of inorganic Hg compounds. The species of Hg being lost from the soil was not determined. However, work with these soils (Rogers 1977, 1976) has shown that the rate of Hg being transformed into a volatile organic compound (methylmercury) is not sufficient to account for the amounts of Hg lost. Other investigators have shown that elemental Hg is the species being volatilized from treated soils (Alberts et al., 1974; Kimura and Miller, 1964; Hitchcock and Zimmerman, 1957). Whether the reason for this loss was the result of chemical or biochemical reduction of Hg was not determined. However, the percent clay and/or organic matter in the soil does mediate the loss rate.

The data presented here clearly show that there can be large, unsuspected losses of Hg from amended soils. In addition, this loss of Hg is not related to nor would it be detected in experiments designed to detect the transformation of Hg compounds into organic species. These data also indicate

methods which can be used to decrease the volatile loss of Hg from contaminated sites. That is, clay and/or organic material could be added to the soil or the available Hg could be bound as HgS by additions of sulfur. Both treatments would result in a substantial decrease in the volatile loss of Hg, especially the sulfur treatment.

LITERATURE CITED

1. Alberts, J. J., J. E. Schindler, R. W. Miller, and D. E. Nutter, Jr. Elemental Mercury Evolution Mediated by Humic Acid. Science 184:895-897, 1974.

2. Avotins, P., and E. A. Jenne. The Time Stability of Dissolved Mercury in Water Samples II. Chemical Stabilization. J. Environ. Qual. 4:515-519, 1975.

3. Braman, R. D., and D. L. Johnson. Selective Adsorption Tubes and Emission Techniques for Determination of Ambient Forms of Mercury in Air. Environ. Sci. Tech. 8:996-1003, 1974.

4. Hadeishi, T., and R. D. McLaughlin. Isotope Zeeman Atomic Absorption: A New Approach to Chemical Analysis. Amer. Lab. 7:57-61, 1975.

5. Hitchcock, A. E., and P. W. Zimmerman. Toxic Effects of Vapors of Mercury and of Compounds of Mercury on Plants. Ann. N.Y. Acad. Sci. 65:474-497, 1957.

6. Kimura, Y., and V. L. Miller. The Degradation of Organomercury Fungicides in Soil. Agri. and Food Chem. 12:253-257, 1964.

7. Rogers, R. D. Abiological Methylation of Mercury in Soil. J. Environ. Qual. 6:463-466, 1977.

8. Rogers, R. D. Methylation of Mercury in Agricultural Soils. J. Environ. Qual. 5:454-458, 1976.